

High Voltage Electrolyte for Lithium Batteries

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Argonne National Laboratory

*Vehicle Technologies Program
Annual Merit Review and Peer Evaluation Meeting*

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Project ID #: ES113

Project Overview

Timeline

- Project start date: FY10
- Project end date: FY14
- Percent complete: 25%

Barriers

- Battery life: conventional organic carbonate electrolytes oxidatively decompose at high potential ($> 4.5\text{V}$ vs Li^+/Li)
- Battery performance: poor oxidation stability of the electrolyte limits the battery energy density
- Battery Abuse: safety concern associated with high vapor pressure, flammability and reactivity

Budget

- Total project funding
 - 100% DOE funding
- Funding received in FY11: \$300K
- Funding for FY12: \$400K

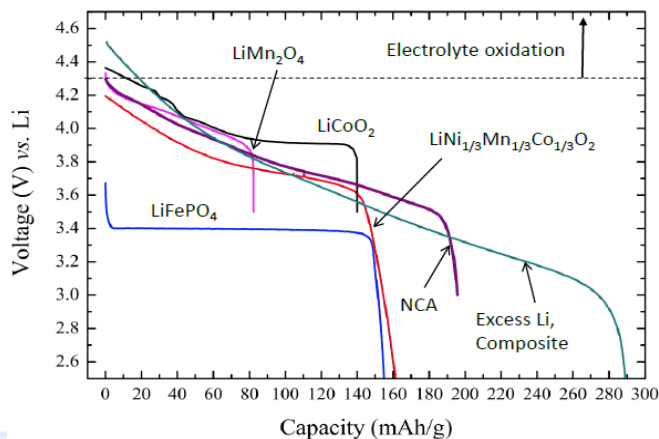
Partners

- US Army Research Lab – Interaction
- Dr. Larry Curtiss – Theoretical modeling
- Daikin Chemical Company - Materials
- Saft and ConocoPhillips - Electrode
- Project Lead: Zhengcheng Zhang

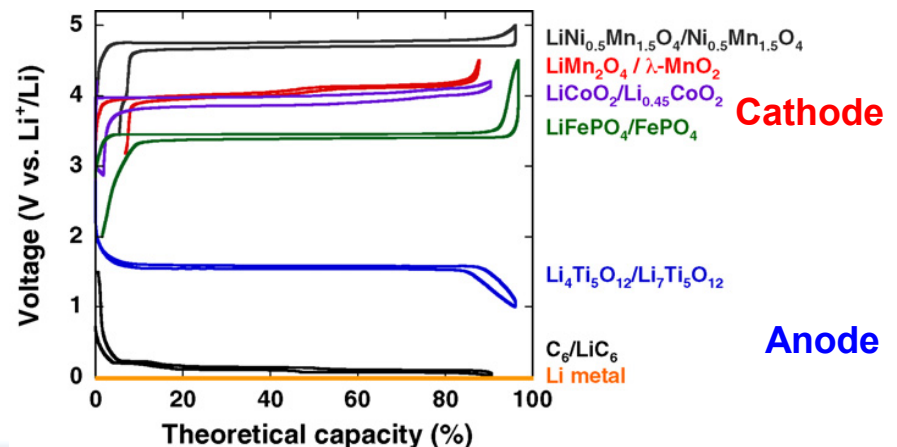
Project Objective

- ❑ The objective of this project is to develop advanced electrolyte materials that can significantly improve the electrochemical performance without sacrificing the safety of lithium-ion battery using high voltage high energy cathode materials to enable large-scale, cost competitive production of the next generation of electric-drive vehicles.
- ❑ To develop electrolyte materials that can tolerate high charging voltage ($>5.0\text{V}$ vs Li^+/Li) with high compatibility with anode material providing stable cycling performance for high voltage cathode including 5V LNMO cathode and high energy LMR-NMC cathode recently developed for high energy high power lithium-ion battery for PHEV and EV applications.
- ❑ FY11's objective is to identify and screen several high voltage electrolyte candidates including sulfone, silicon-based and fluorinated compounds with the aid of quantum chemistry modeling and electrochemical methods and to investigate the cell performance of the selected electrolytes in LNMO/LTO and LNMO/graphite chemistries.

Increase capacity



Increase voltage



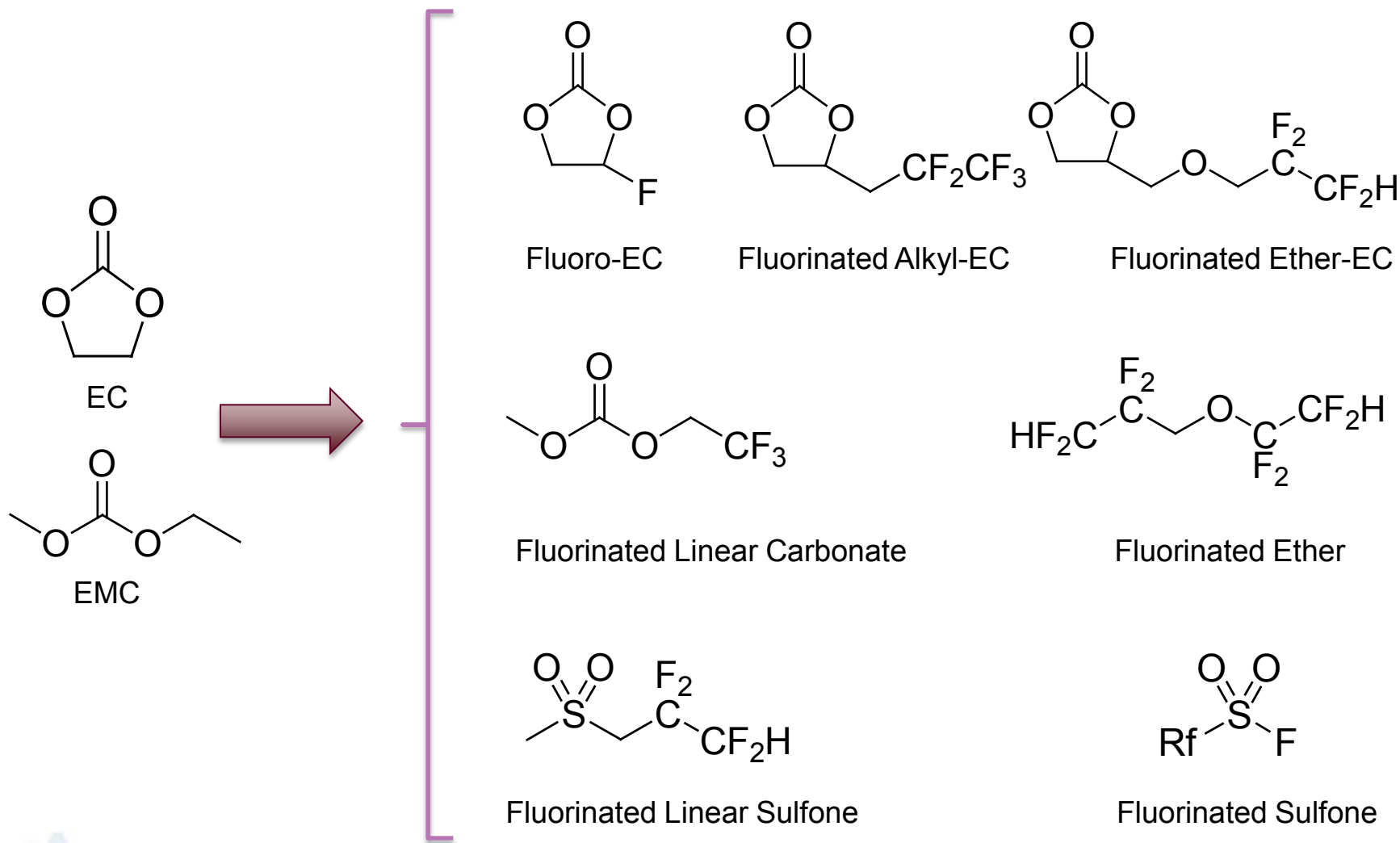
Approach

- ❑ R&D groups all over the world work on improving electrodes materials in order to maximize both energy and power density of Li batteries. High voltage cathode ($\text{Li}[\text{MMn}]_2\text{O}_4$, $\text{M}=\text{Ni}, \text{Cr}, \text{Cu}$) and high capacity layered cathode ($\text{Li}[\text{NiMnCo}]\text{O}_2$) red-ox potentials approach 5.0V and 4.6V vs Li^+/Li . Conventional alkyl carbonates/ LiPF_6 tend to be oxidized around 4.5V. Development of high voltage electrolyte is urgent and challenging.
- ❑ Our overall approach for high voltage electrolyte research is to first design, synthesize and characterize high oxidation stable solvent candidates with the aid of theoretical calculation method; then screen the electrochemical properties of the synthesized using cyclic voltammetry and validate their oxidation stability using high voltage and high capacity cathode Li metal or LTO cells. Tailored electrolyte additive will be developed coupled with main electrolyte to enable the graphite cells is the ultimate target.
- ❑ High voltage electrolyte research will be integrated with high voltage/capacity cathode project in DOE ABR program. Various new solvent systems including sulfones, silane, fluorinated esters, fluorinated ethers and ionic liquids. Synergy effect of electrolyte containing hybrid solvents will also explored to enable the high energy high power lithium-ion battery for PHEV and EV applications.



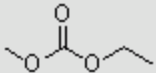
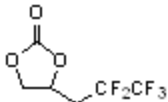
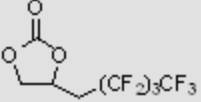
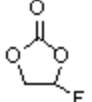
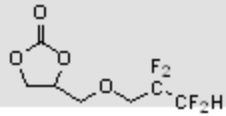
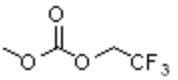
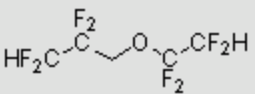


Technical Accomplishments and Progress

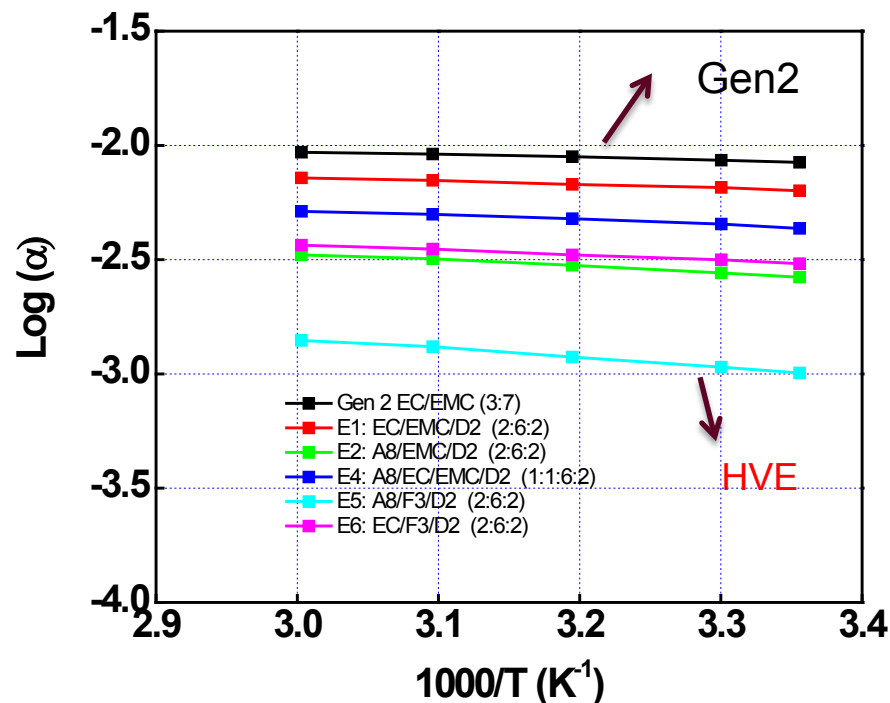
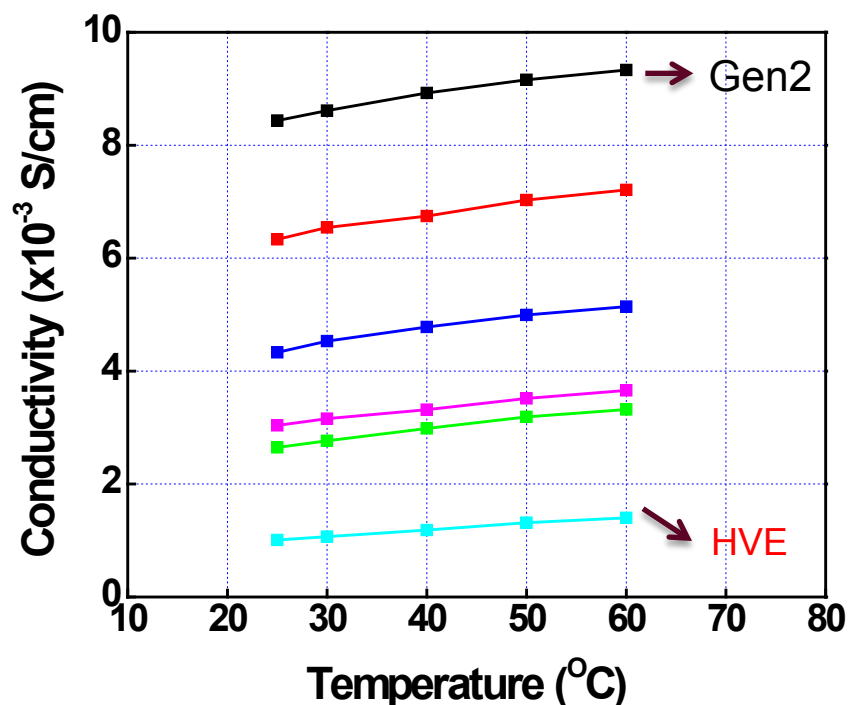
Argonne's Fluorinated Compounds as High Voltage Electrolytes (HVEs)



DFT Calculation to Predict the Oxidation Stability of Fluorinated Carbonate Compounds

Code Name	Chemical Structure	P_{ox}^a / V	P_{red} / V
EC		6.91	1.43
PC		6.80	1.35
EMC		6.63	1.30
A8		6.97	1.69
A9		7.02	-
FEC		7.16	1.63
HFEEC		6.93	1.50
F3		7.10	1.58
D2		7.29	1.82

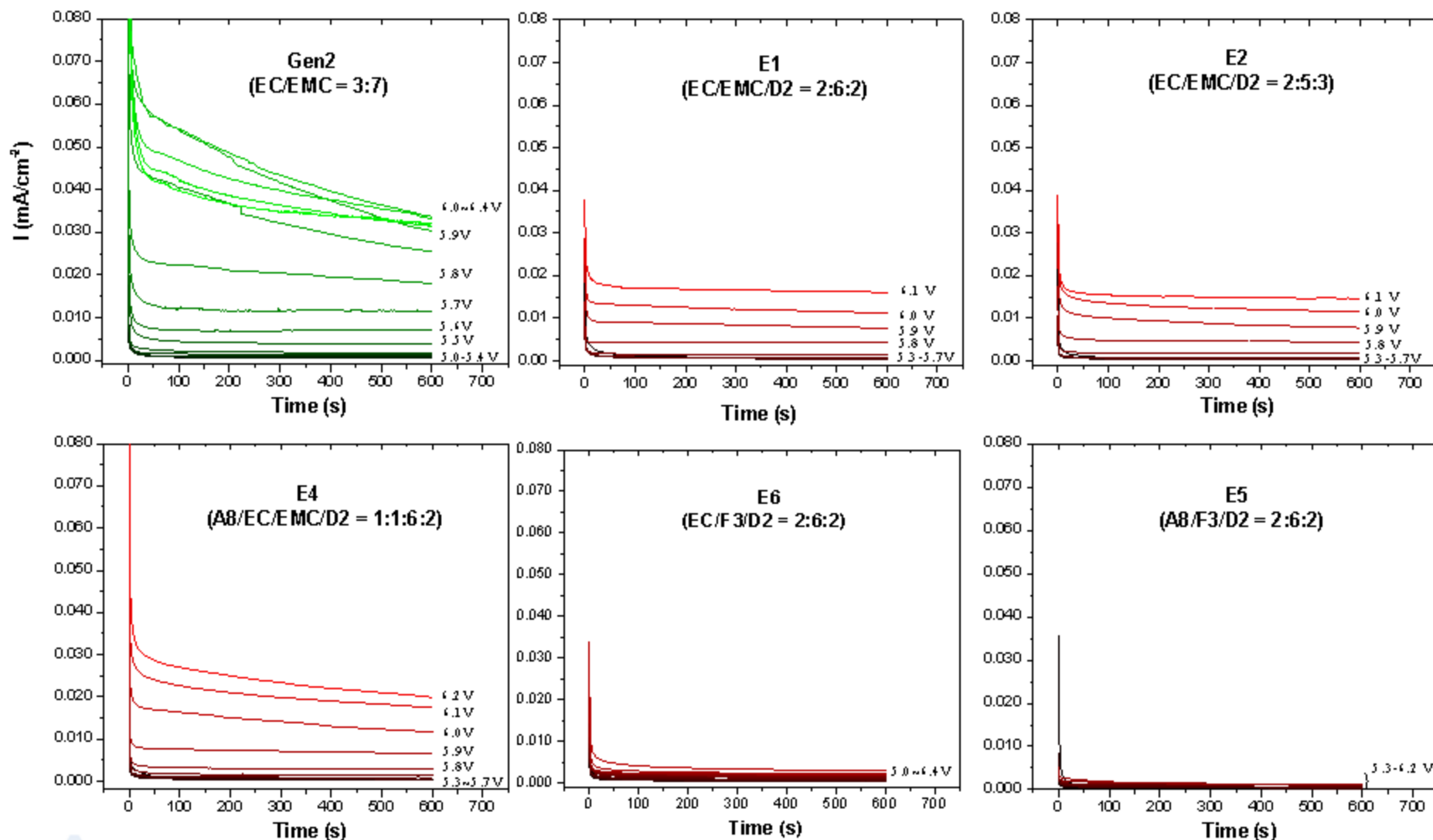
Li⁺ Conductivity of High Voltage Electrolyte Candidates



- Compared to Gen 2, all fluorinated electrolytes are less conductive. EC/EMC/D2 showed the highest ambient conductivity of $6.5 \times 10^{-3} \text{ S/cm}$ among all the fluorinated electrolyte candidates.
- Addition of A8, F3 and/or D2 reduces the conductivity.
- A8/F3/D2 formulation shows the lowest conductivity due to the overall low dielectric constant and high viscosity (see Technical Backup Slides).

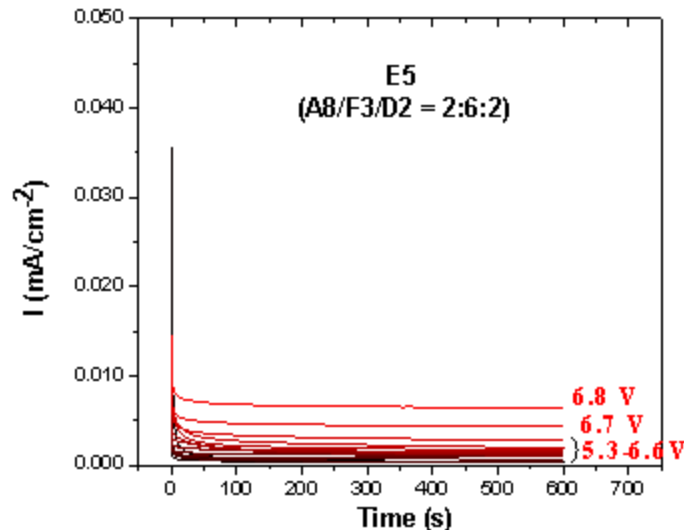
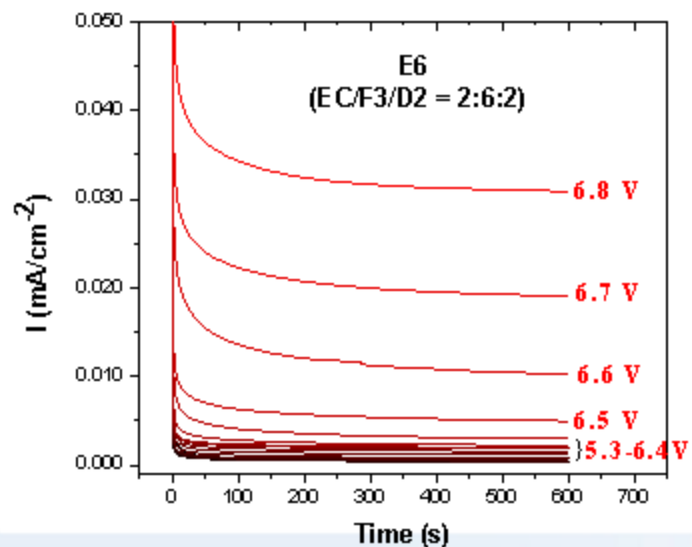
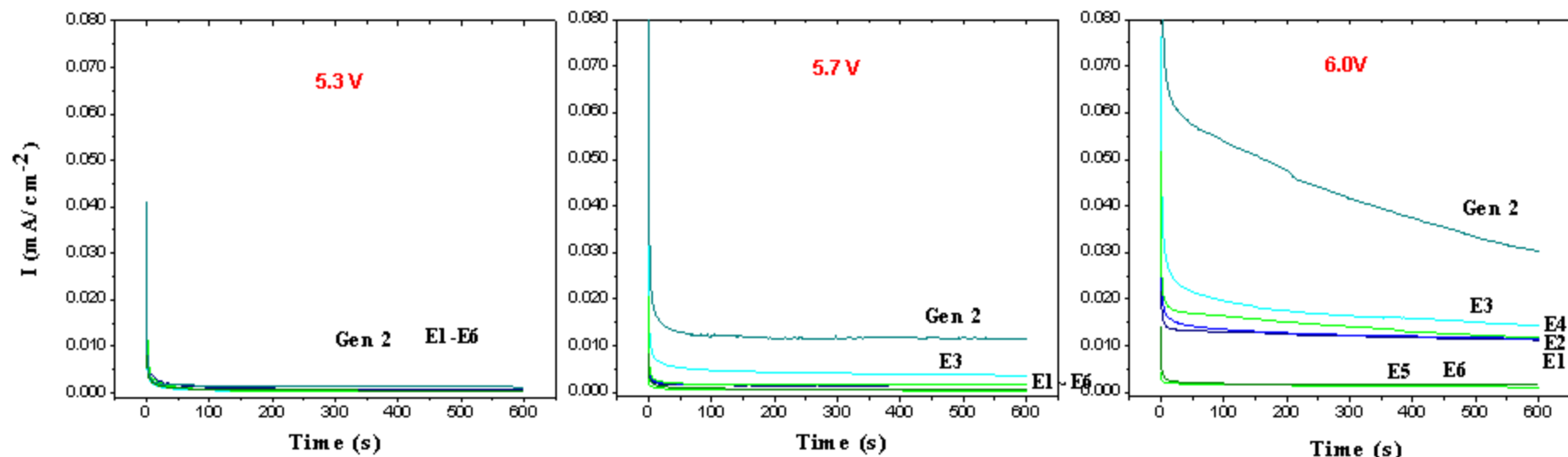


Electrochemical Oxidation Stability of Fluorinated Carbonate Electrolyte: Floating Test*



* Three-electrode electrochemical cell with Pt as working electrode and Li as reference and counter electrode.

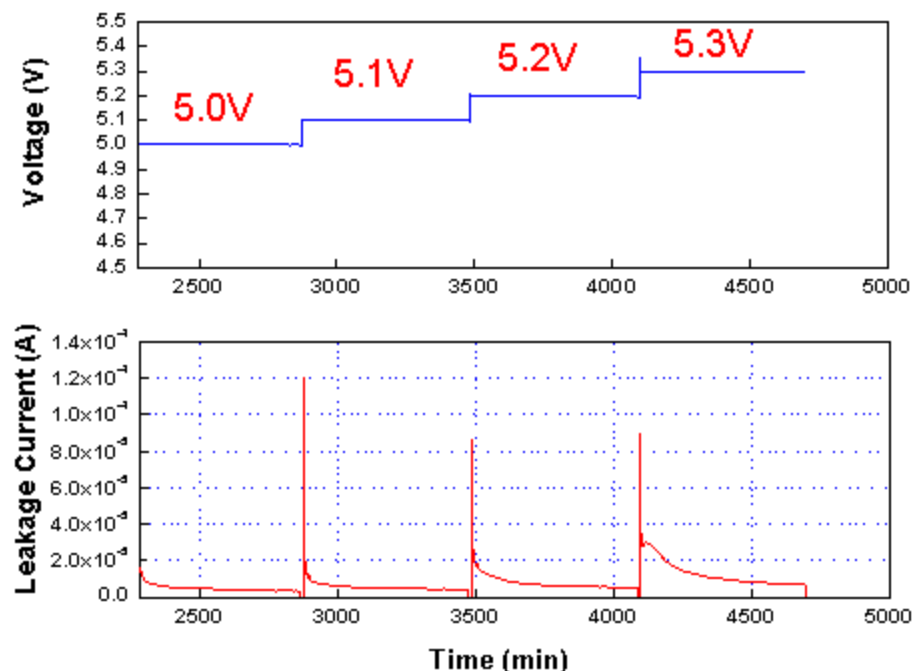
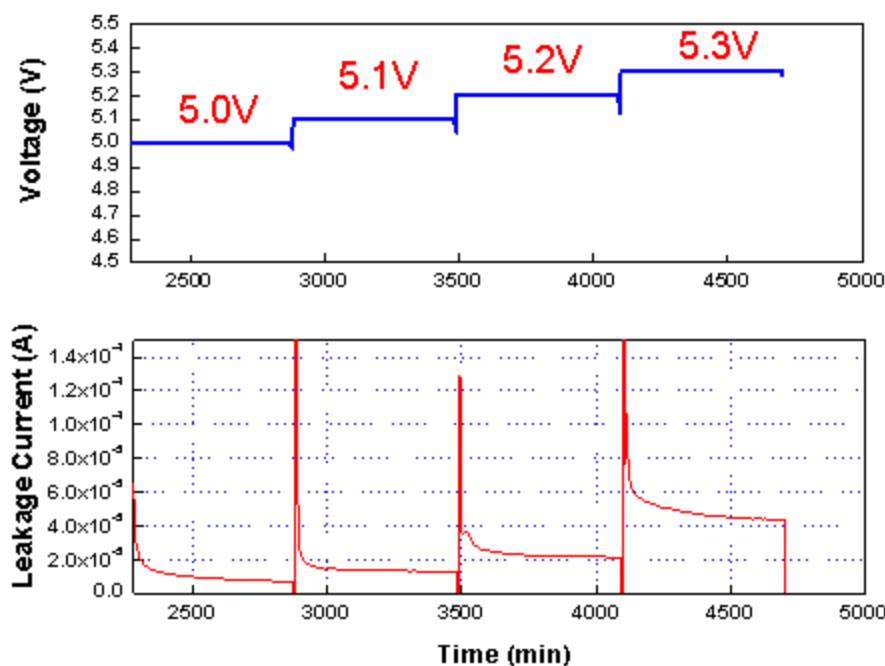
Electrochemical Oxidation Stability of Fluorinated Carbonate Electrolyte: Floating Test



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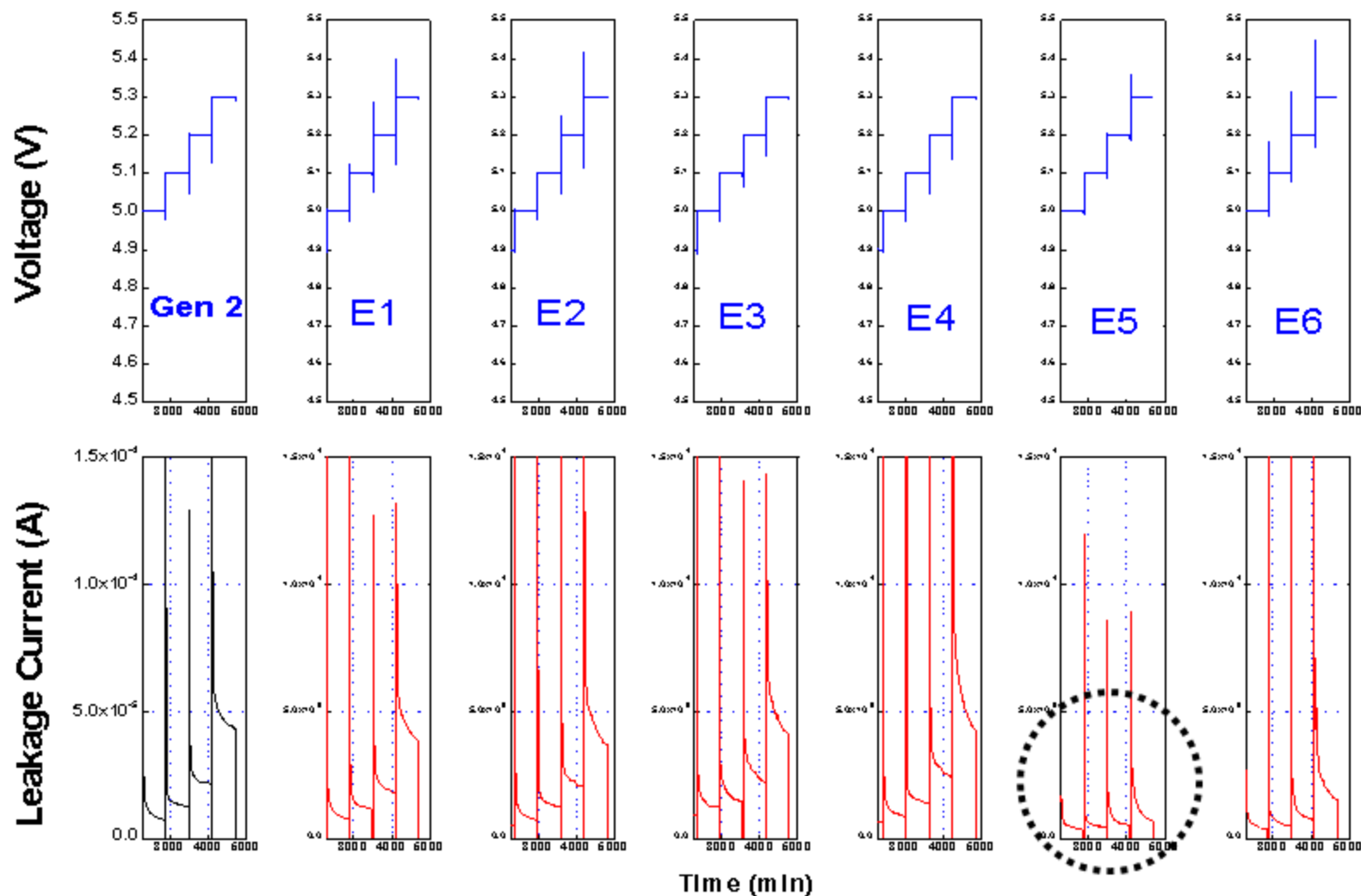
1.2M LiPF₆ EC/EMC 3/7

E5: All Fluorinated Electrolyte



- * (1) Working electrode: LiNi_{0.5}Mn_{1.5}O₄ /Carbon Black/Binder: 84%/8%/8% in weight
(2) Electrode disc area: 1.6cm²
(3) Reference electrode: Li metal
(4) CC-CV charge the LNMO/Li cell with C/10 rate to 5.0V, 5.1V, 5.2V and 5.3V, respectively. Maintain at each voltage for 10h to observe the leakage current.

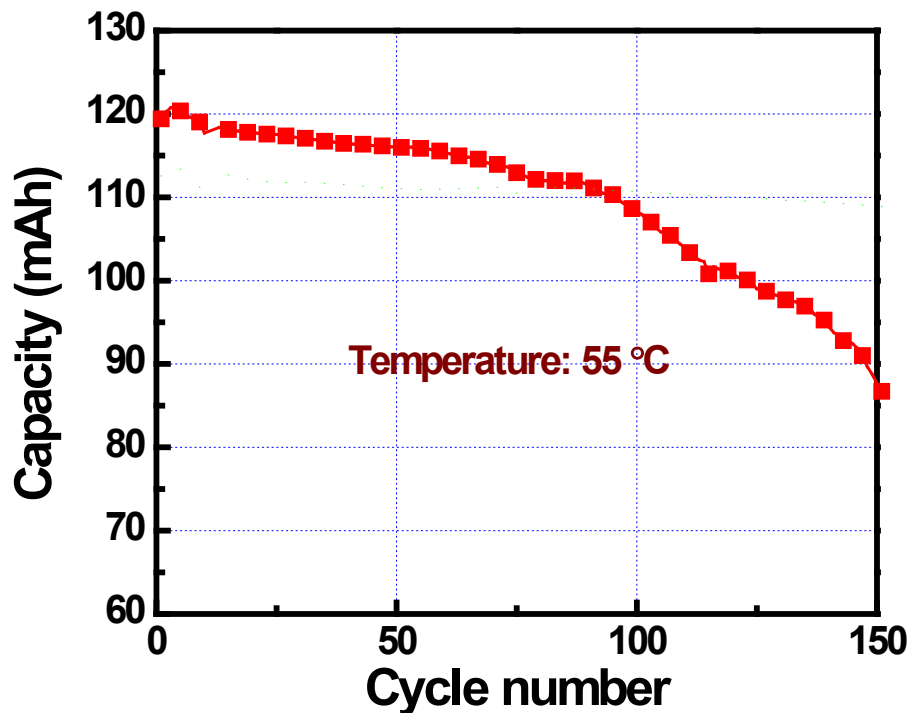
Electrochemical Oxidation Stability of Fluorinated Carbonate Electrolyte: Floating Test*



Floating Test Leakage Current Summary

Electrolyte	Formulation	Leakage Current (A)			
		5.0V	5.1V	5.2V	5.3V
Gen2	EC/EMC (3/7)	1.0×10^{-5}	1.3×10^{-5}	2.2×10^{-5}	4.5×10^{-5}
E1	EC/EMC/D2 (2/6/2)	0.9×10^{-5}	1.2×10^{-5}	2.0×10^{-5}	4.3×10^{-5}
E2	EC/EMC/D2 (2/5/3)	0.8×10^{-5}	1.2×10^{-5}	2.1×10^{-5}	4.3×10^{-5}
E3	A8/EMC/D2 (2/6/2)	1.2×10^{-5}	1.7×10^{-5}	2.5×10^{-5}	4.5×10^{-5}
E4	A8/EC/EMC/D2 (1/1/6/2)	1.0×10^{-5}	1.5×10^{-5}	2.7×10^{-5}	5.1×10^{-5}
E5	A8/F3/D2 (2/6/2)	0.4×10^{-5}	0.5×10^{-5}	0.7×10^{-5}	1.0×10^{-5}
E6	EC/F3/D2 (2/6/2)	0.4×10^{-5}	0.6×10^{-5}	0.9×10^{-5}	2.0×10^{-5}

High Reactivity of Conventional Electrolyte in LNMO Cell at High Temperature 55 °C



Cell Testing Condition:

Electrolyte: 1.2M LiPF_6 in EC/EMC (3/7)

LNMO/Li

Cut-off voltage: 3.2~4.95 V

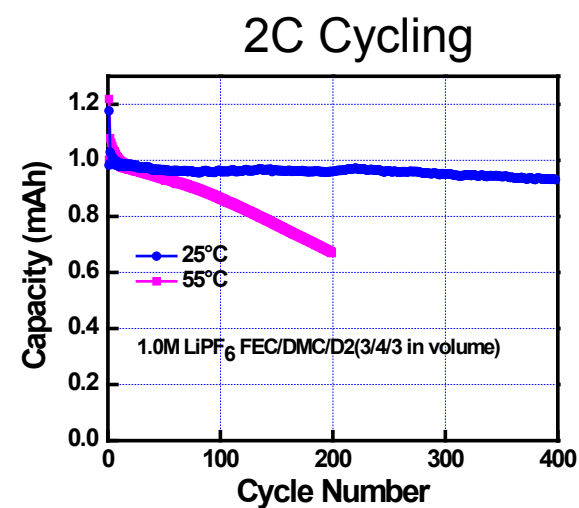
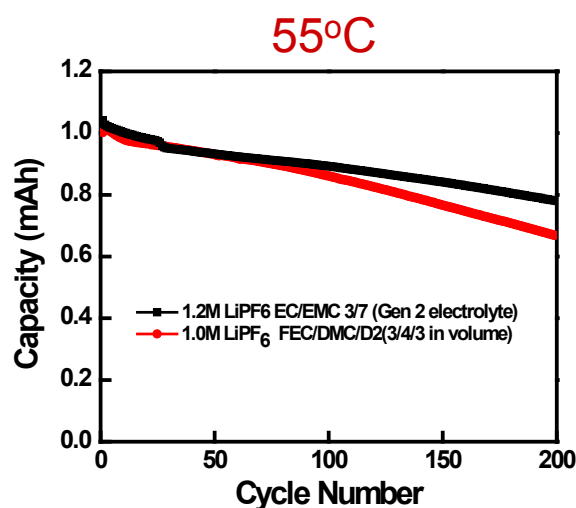
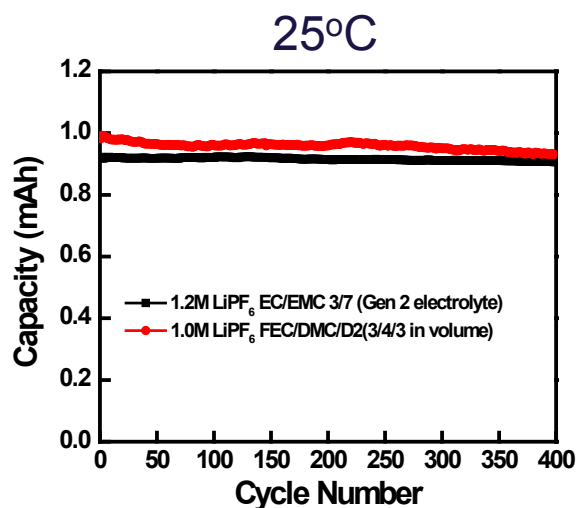
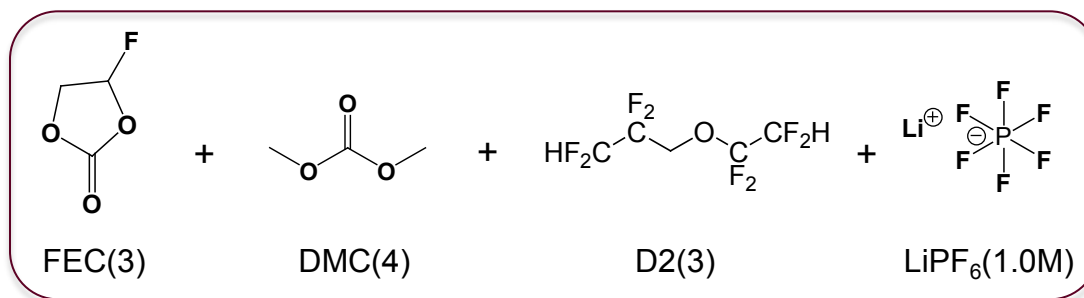
Chg-dchg current rate: C/10

Separator: Celgard® 2325

Testing vehicle: CR 2032

- ❑ The capacity of LNMO/Li cell degrades dramatically (>20% loss of its initial capacity) even in 150 cycles.
- ❑ Although cathode (active material, binder) and other factors (separator, Li anode), electrolyte is the main contributor to the poor electrochemical performance.

F-EC Electrolyte Performance in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ / $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Cell at Elevated Temperature

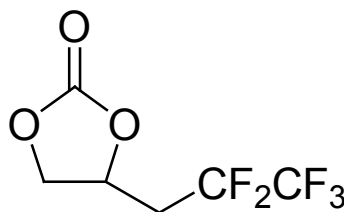
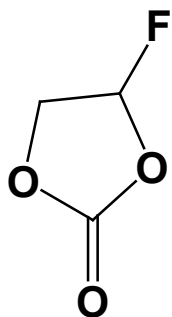
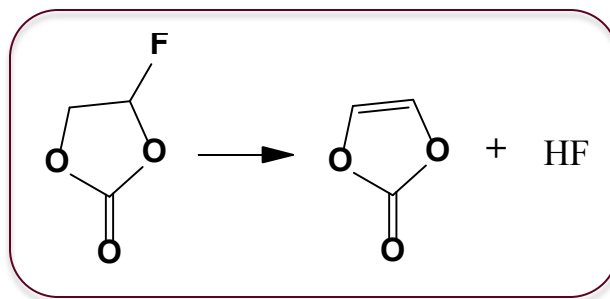


Cut-off voltage: 2.0-3.45V

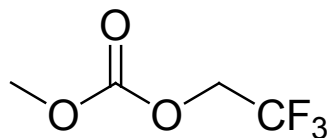
- Fluorinated-EC/ether electrolyte showed excellent cycling performance at RT;
- However at elevated temperature, both cell started to degrade at 100th cycle due to the instability of the electrolyte (FEC-electrolyte showed quick degradation);
- With accelerated C-rate, the F-EC electrolyte performs well but degrade fast at 55° C (right figure).

New Fluorinated Electrolytes To increase the Thermal/Chemical Stability

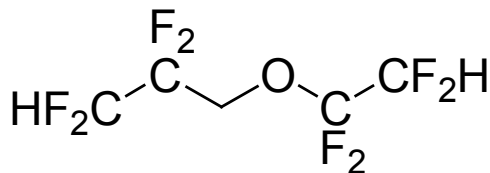
FEC Thermal decomposition:



(A8)



(F3)



(D2)



LNMO/LTO Cycling Performance Improvement

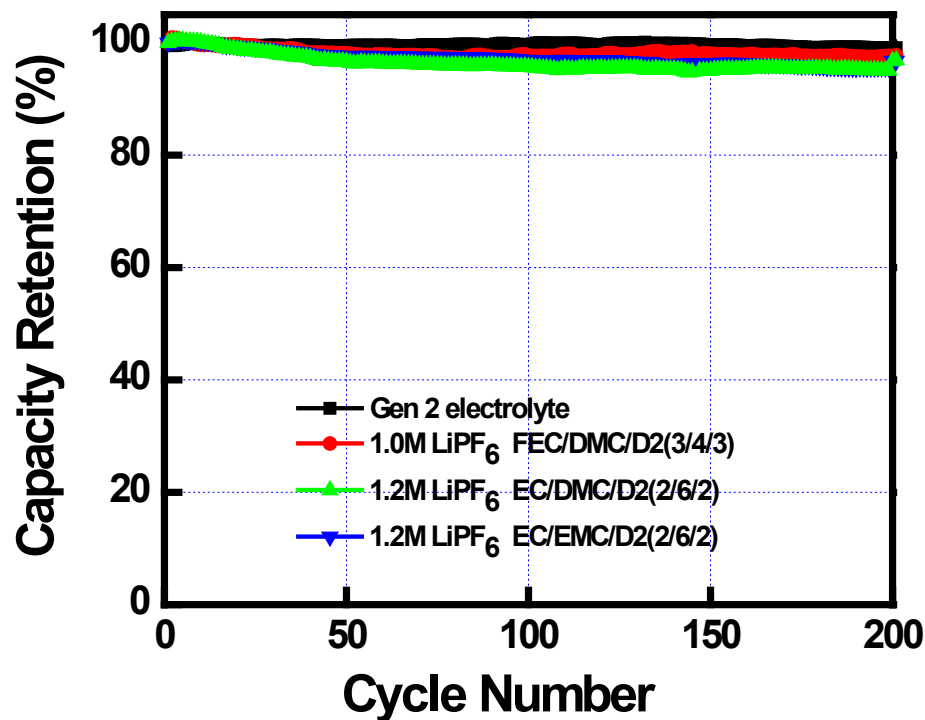
Gen 2 electrolyte (1.2 M LiPF₆ EC/EMC (3/7))

1.0M LiPF₆ FEC/DMC/D2(3/4/3)

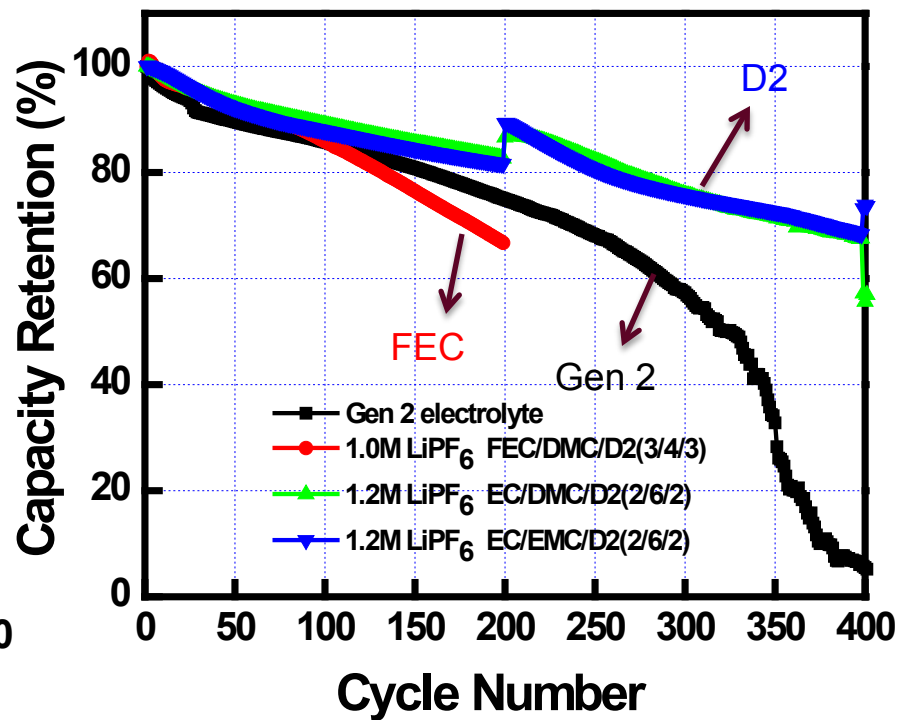
1.2M LiPF₆ EC/DMC/D2(2/6/2)

1.2M LiPF₆ EC/EMC/D2(2/6/2)

25°C



55°C



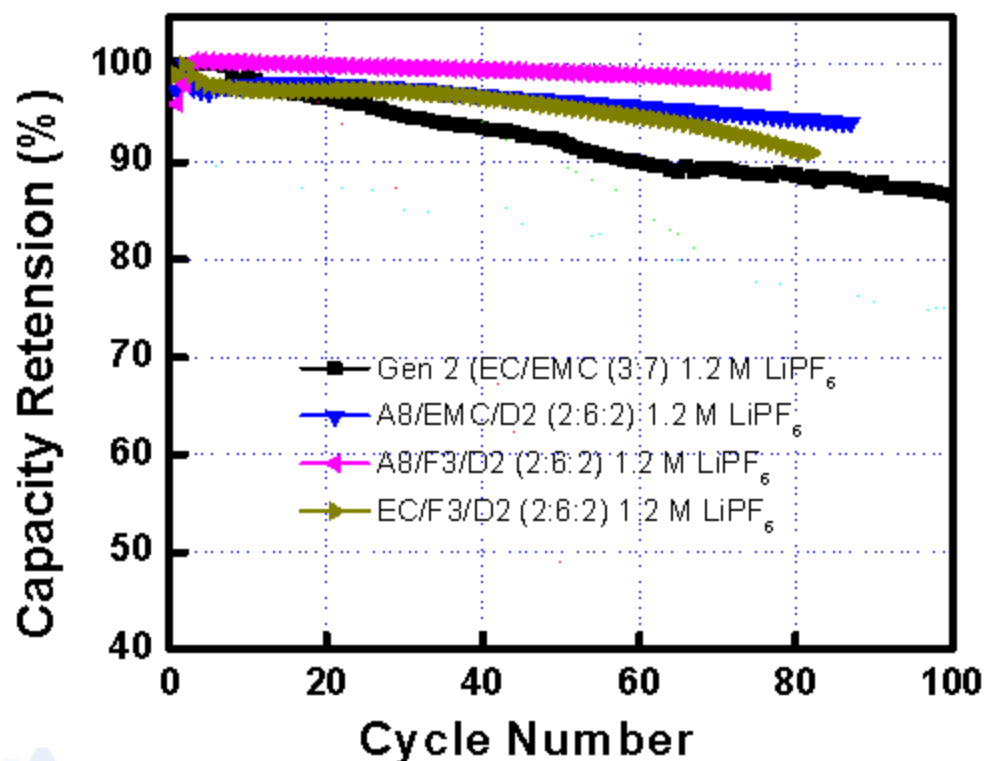
Cycling Performance of LNM0/LTO Cell with Fluorinated Electrolytes at 55 °C

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNM0)/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO)

High temperature: 55 °C

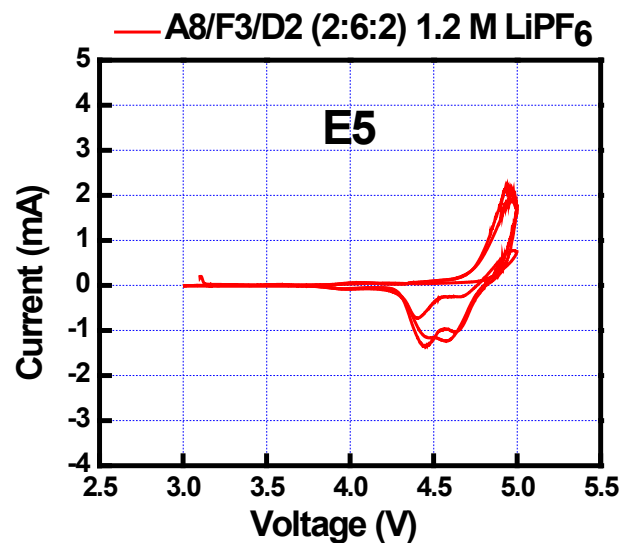
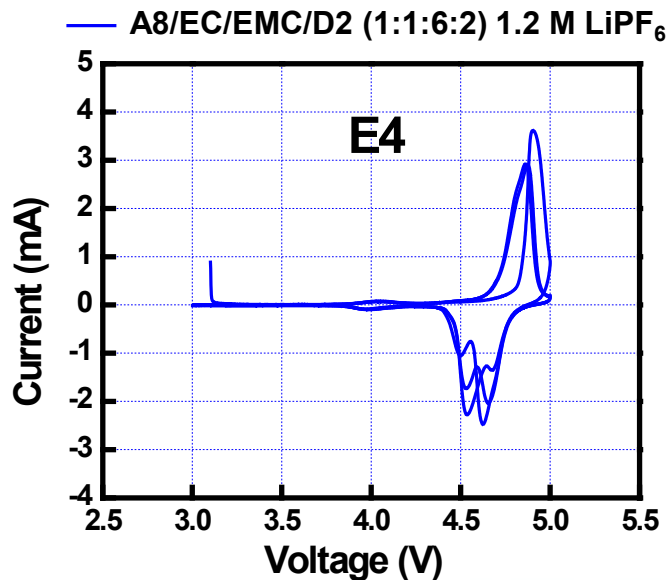
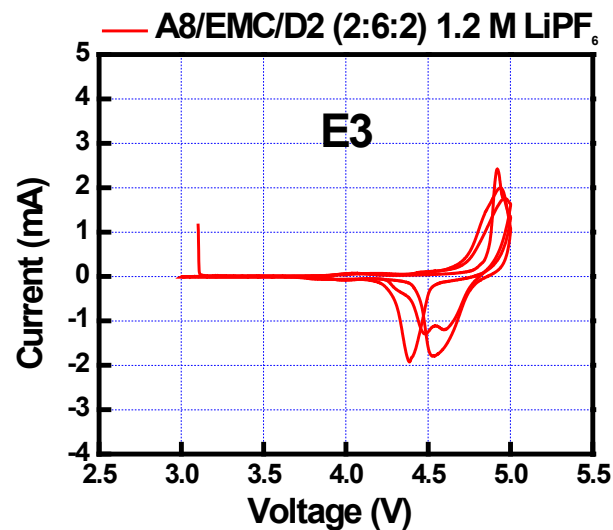
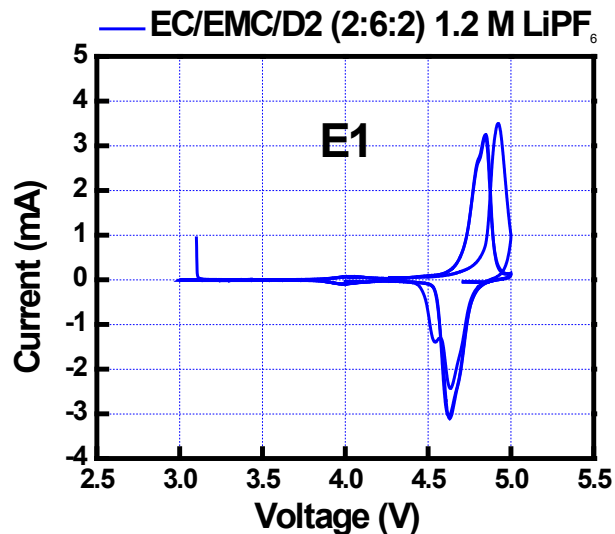
Current density: C/10 for formation, and C/2 for cycling

Cut-off voltage: 2.0-3.45 V



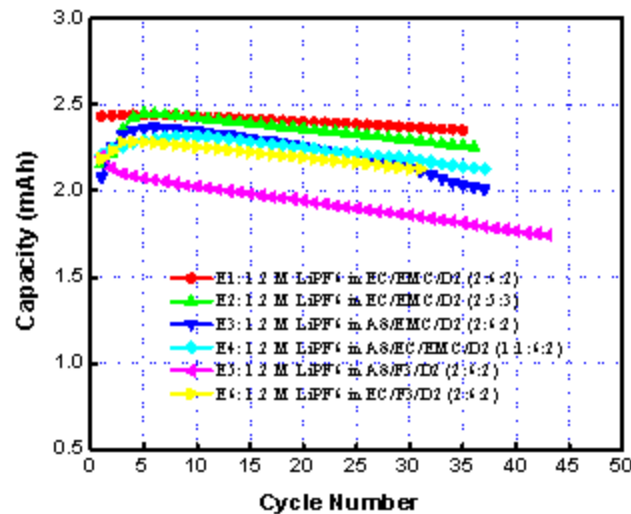
- The Gen2 electrolyte cell lost 13% of initial capacity in 100 cycles;
- A8/EMC/D2 electrolyte showed improved cycling performance than Gen2;
- All-fluorinated electrolyte A8/F3/D2 showed the best capacity retention among all the fluorinated electrolytes.

First Cycle Potentiostatic Profile of LNMO/Graphite Cell

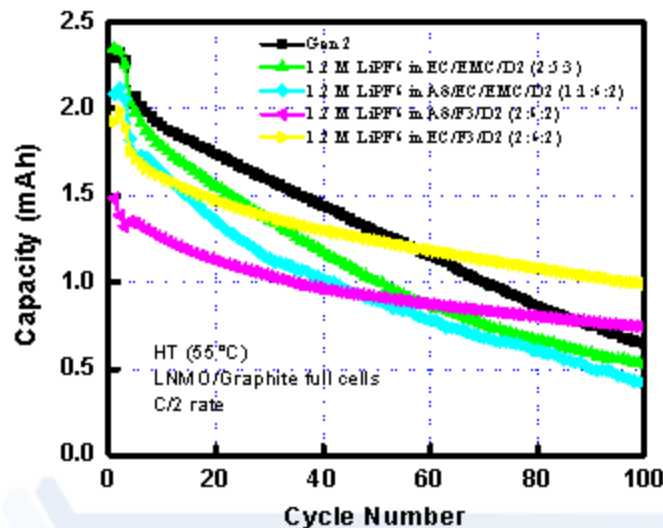
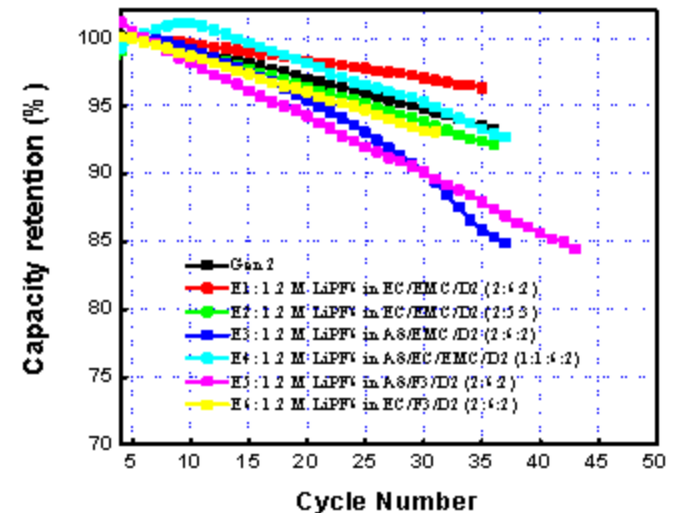


LNMO/Graphite Cell Performance

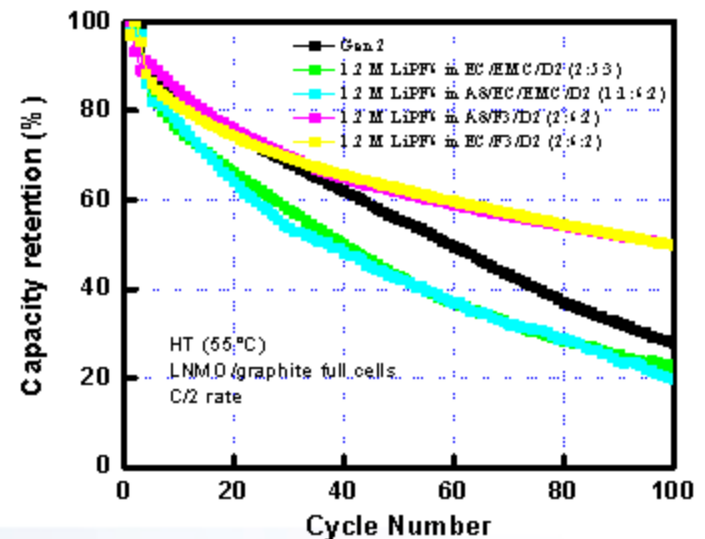
Cycling performance, Room temperature (25°C), C/10, cutoff voltage : 3.5-4.9 V



Room Temp.
(25°C)



High Temp.
(55°C)



Collaboration and Coordination with Other Institutions

Partners:

- **Center of Nano-Materials at Argonne (DOE Lab)**
Dr. Larry Curtiss for theoretical calculation of red-ox potentials by quantum chemical methods.
- **Daikin Industries, Ltd. (Chemical Industry)**
Dr. Meiten Koh for the electrolyte material synthesis discussions.

Collaborators:

- **US Army Research Laboratory (DOD Lab)**
Dr. Richard Jow and Kang Xu for information and technical exchanges.
- **ConocoPhillips, Saft, and EnerDel (Battery Industry)**
High voltage spinel cathode, LTO and A12 graphite anode supply.

Proposed Future Work

- ✓ During the rest of the FY12, our research will continue the exploration of the fluorinated carbonate-based electrolytes as high voltage electrolytes:
 - Scientific write-up for publication in peer-reviewed journals;
 - Optimal formulation including hybrid electrolyte approach will be sought for best performance (Power, Cycling);
 - New fluorinated carbonate solvent design, synthesis, characterization and electrochemical performance evaluation;
 - Tailored SEI additives to enable the graphite high voltage cell especially at elevated temperatures.

- ✓ In the year of FY13, we propose the following work in order to achieve the milestones and the final goal of this project:
 - Design and synthesis of fluorinated non-carbonate solvents as backup high voltage electrolytes;
 - Electrochemical properties investigation of new electrolyte systems.


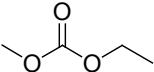
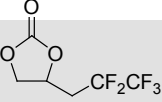
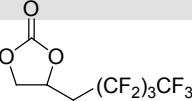
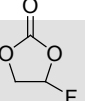
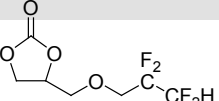
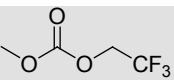
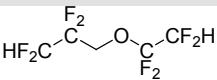
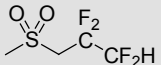
Summary

PHEV and EV batteries face many challenges including energy density, calendar life, cost, and abuse tolerance. The approach of this project to overcome the above barriers is to develop highly stable electrolyte materials that can significantly improve the high voltage cell performance without sacrificing the safety to enable large-scale, cost competitive production of the next generation of electric-drive vehicles.

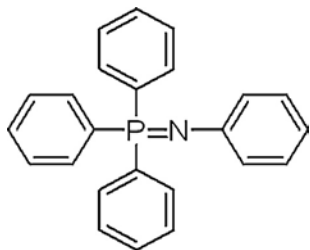
- ❑ Argonne has initiated the fluorinated carbonate-based electrolytes as high voltage electrolyte to improve the battery energy density by enabling the high voltage cells;
- ❑ Determination of electrolyte oxidation stability was established by floating test using both inert working electrode and high voltage cathode;
- ❑ Fluorinated carbonate electrolytes showed promising performance both in theory and in real cell: superior capacity retention at elevated temperature compared to the conventional one using 5V spinel LNMO/LTO cell.
- ❑ Argonne's fluorinated carbonate electrolytes improved the cell capacity fading for graphite cells. FY12 plan was proposed to address the low first cycle capacity loss through additive approach.

Technical Back-Up Slides

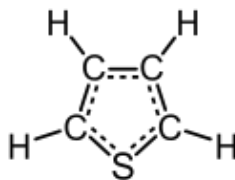
Physical Properties of Some Fluorinated Solvents

Code Name	Chemical Structure	F.W.	Viscosity 25°C mPa·s	Dielectric Constant	Density g·cm ⁻³	Flash point / °C	Boiling point / °C
EC		88	1.90 (40°C)	90	1.32	160	244
EMC		92	0.89	2.9	1.01	21	107
A8		220	solid	-	-	>80	-
A9		320	solid	-	-	>80	-
FEC		106	4.0	105.7	1.55	129	210
HFEEC		232	38	87.2	1.50	>80	-
F3		158	1.1	7.3	1.36	33.3	93
D2		232	1.60	6.4	1.53	-	92
S2		210	11.0	27.9	1.47	-	150-160

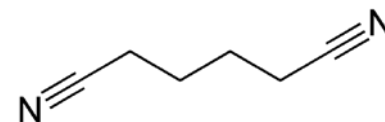
High Voltage Electrolyte Development Status



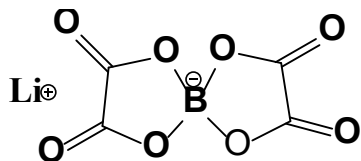
N-(triphenylphosphoranylidene)
Aniline (TPPA)



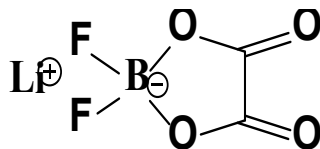
Thiophene



1,4-Dicyanobutane
(Adiponitrile)
1,10-Dicyanodecane
1,8-Dicyanooctane
1,6-Dicyanohexane
1,5-Dicyanopentane

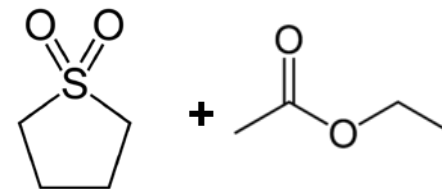


Lithium Bis(oxalato) Borate



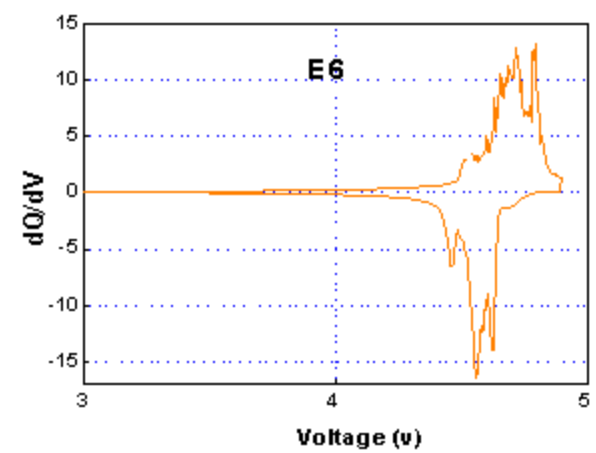
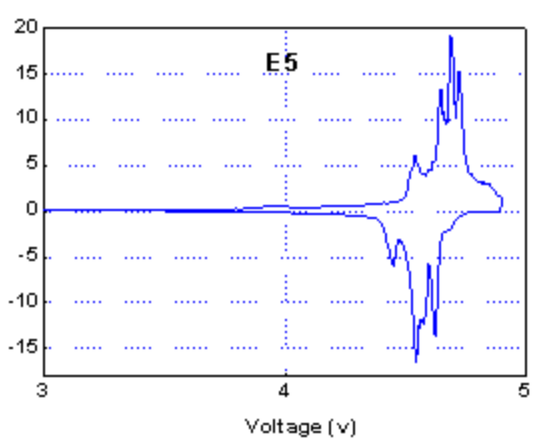
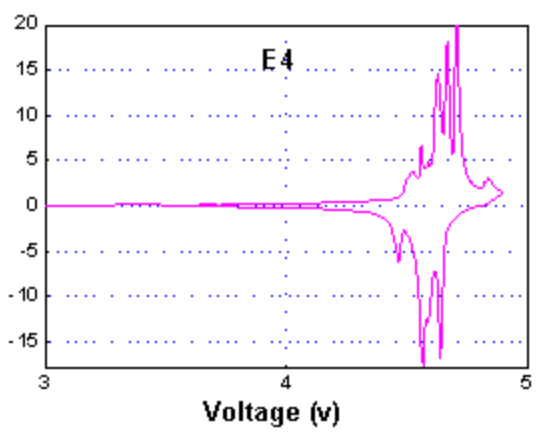
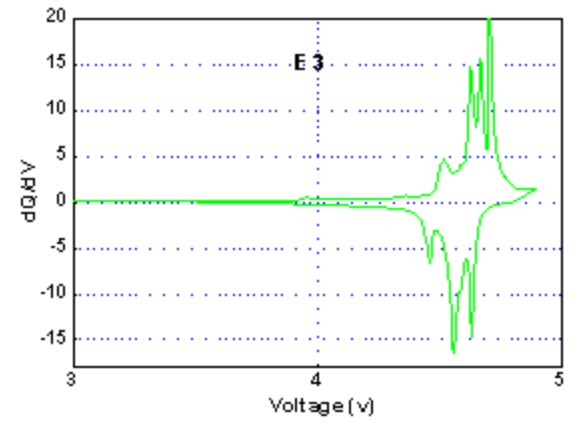
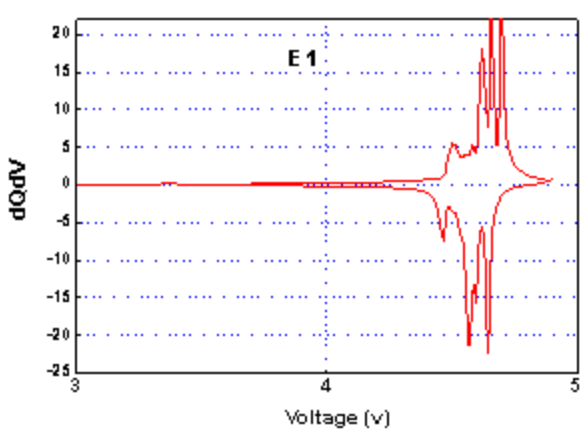
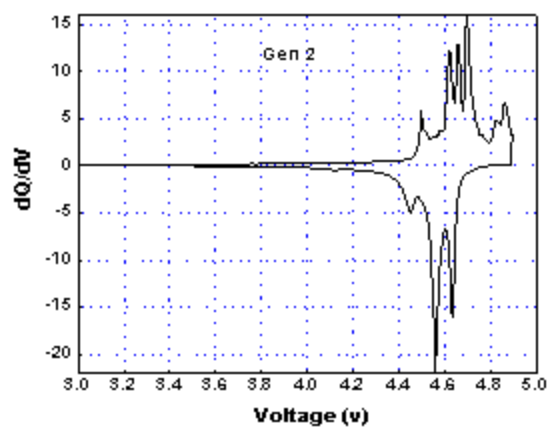
Lithium Difluoro(oxalato) Borate

- 1) Electrochimica Acta 56 (2011) 5195–5200
- 2) Electrochemistry Communications 11 (2009) 1900–1903
- 3) Journal of The Electrochemical Society, 156 1 A60-A65 2009
- 4) Journal of The Electrochemical Society, 157 6 A748-A752 2010
- 5) Journal of Power Sources 179 (2008) 770–779
- 6) Journal of Power Sources 196 (2011) 2251–2254
- 7) Electrochimica Acta 52 (2007) 3870–3875



Surface Coating
(Nano SiO₂-Coated
LiNi_{0.5}Mn_{1.5}O₄)

First Cycle Differential Capacity Profile of LNM0/Graphite Cell with Fluorinated Electrolytes



EC/EMC (3:7) 1.2 M LiPF₆

E1: EC/EMC/D2 (2:6:2) 1.2 M LiPF₆
 E2: EC/EMC/D2 (2:5:3) 1.2 M LiPF₆
 E3: A8/EMC/D2 (2:6:2) 1.2 M LiPF₆

E4: A8/EC/EMC/D2 (1:1:6:2) 1.2 M LiPF₆
 E5: A8/F3/D2 (2:6:2) 1.2 M LiPF₆
 E6: EC/F3/D2 (2:6:2) 1.2 M LiPF₆

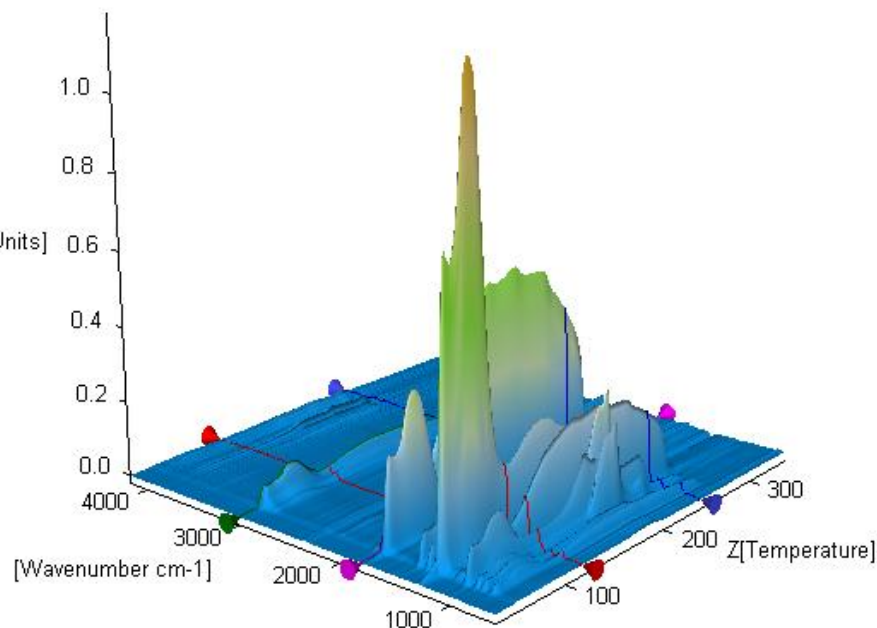


DSC-TGA-FTIR Analysis of High Voltage Electrolytes

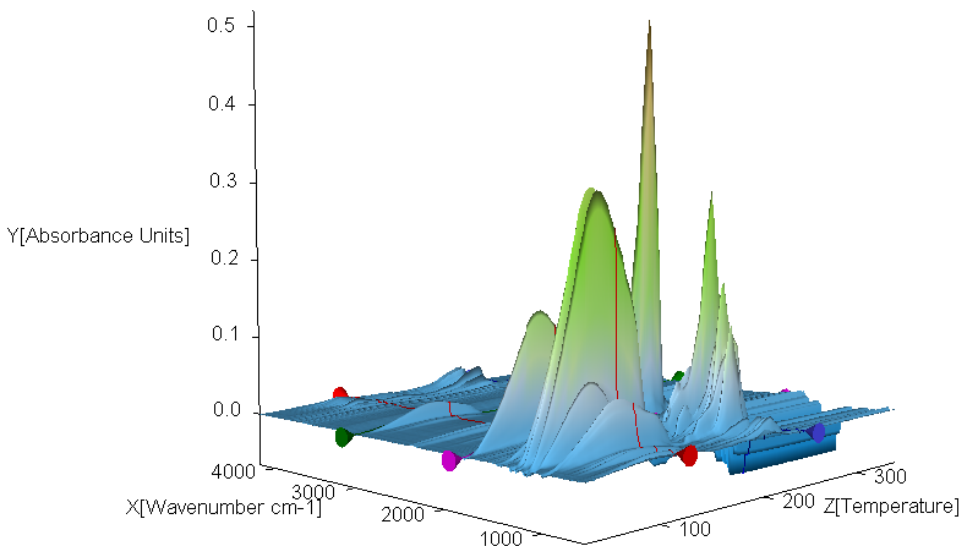
Gen2 Electrolyte
1.2M LiPF₆ EC/EMC 3/7



Y[Absorbance Units]



E5 Electrolyte
1.2M LiPF₆ A8/F3/D2 (2:6:2)



Performance of LNMO/Graphite Full Cell at Room Temperature

High rate (C/3) cycling performance in terms of capacity retention
Room temperature, C/10, cutoff voltage: 3.5-4.9 V

